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Fracturing fluids for delayed flow back operations

(57) A fracturing fluid composition comprises a hydratable polymer, a water wetting agent, a clay control agent, a microbe growth control agent, a scale inhibitor and a breaking agent. The fracturing fluid can be used to fracture a subterranean formation and be permitted to stay within the formation for 28 days or more before being back flowed. The fluid will not cause deterioration of the formation by causing clay swelling, H_2S generation, oil wetting the formation, or plugging the formation with slime or scale. Preferably the fracturing fluid is free from components that contain sulfur, with the exception of sulphonates. The hydratable polymer is preferably guar crosslinked with a borate ion. The fluid may either be an antibacterial formulation, or it may contain bacteria that will compete with the bacteria downhole, thus preventing proliferation of the undesirable bacteria.

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FRACTURING FLUIDS FOR DELAYED FLOW BACK OPERATIONS

Field of the Invention

The present invention relates to fluids used in fracturing subterranean formations during hydrocarbon recovery operations, and more particularly relates, in one embodiment, to fracturing fluids that remain in the formation for relatively long periods of time.

Background of the Invention

Hydraulic fracturing is a method of using pump rate and hydraulic pressure to fracture or crack a subterranean formation. Once the crack or cracks are made, high permeability proppant, relative to the formation permeability, is pumped into the fracture to prop open the crack. When the applied pump rates and pressures are reduced or removed from the formation, the crack or fracture cannot close or heal completely because the high permeability proppant keeps the crack open. The propped crack or fracture provides a high permeability path connecting the producing wellbore to a larger formation area to enhance the production of hydrocarbons.

The development of suitable fracturing fluids is a complex art because the fluids must simultaneously meet a number of conditions. For example, they must be stable at high temperatures and/or high pump rates and shear rates that can cause the fluids to degrade and prematurely settle out the proppant before the fracturing operation is complete. Various fluids have been developed, but most commercially used fracturing fluids are aqueous based liquids that have either been gelled or foamed. When the fluids are gelled, typically a polymeric gelling agent, such as a solvatable polysaccharide is used. The thickened or gelled fluid helps keep the proppants within the fluid. Gelling can be accomplished or improved by the use of crosslinking agents or crosslinkers that promote crosslinking of the polymers together, thereby increasing the viscosity of the fluid.

The recovery of fracturing fluids may be accomplished by reducing the viscosity of the fluid to a low value so that it may flow naturally from the

formation under the influence of formation fluids. Crosslinked gels generally require viscosity breakers to be injected to reduce the viscosity or "break" the gel. Enzymes, oxidizers, and acids are known polymer viscosity breakers. Enzymes are effective within a pH range, typically a 2.0 to 10.0 range, with increasing activity as the pH is lowered towards neutral from a pH of 10.0. Most conventional borate crosslinked fracturing fluids and breakers are designed from a fixed high crosslinked fluid pH value at ambient temperature and/or reservoir temperature. Optimizing the pH for a borate crosslinked gel is important to achieve proper crosslink stability and controlled enzyme breaker activity.

Fracturing fluids also include additives to help inhibit the formation of scale including, but not necessarily limited to carbonate scales and sulfate scales. Such scale cause blockages not only in the equipment used in hydrocarbon recovery, but also can create fines that block the pores of the subterranean formation. Examples of scale inhibitors and/or scale removers incorporated into fracturing fluids include, but are not necessarily limited to polyaspartates; hydroxyaminocarboxylic acid (HACA) chelating agents, such as hydroxyethyliminodiacetic acid (HEIDA); ethylenediaminetetracetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), nitrilotriacetic acid (NTA) and other carboxylic acids and their salt forms, phosphonates, and acrylates and mixtures thereof.

Fracturing fluids that are crosslinked with titanate, zirconate, and/or borate ions (using compounds which generate these ions), sometimes contain additives that are designed to delay crosslinking. Crosslinking delay agents permit the fracturing to be pumped down hole to the subterranean formation before crosslinking begins to occur, thereby permitting more versatility or flexibility in the fracturing fluid. Examples of crosslink delay agents commonly incorporated into fracturing fluids include, but are not necessarily limited to organic polyols, such as sodium gluconate; sodium glucoheptonate, sorbitol, glyoxal, mannitol, phosphonates, aminocarboxylic acids and their salts (EDTA, DTPA, etc.) and mixtures thereof. Another type of crosslink delay mechanism for borate crosslinked fluids is type, amount, and particle size distribution of

borate mineral particles. An example is the product Fracsal Waterbase available from TBC-Brineadd (Houston, TX).

Other common additives employed in conventional fracturing fluids include crosslinked gel stabilizers that stabilize the crosslinked gel (typically a polysaccharide crosslinked with titanate, zirconate or borate) for a sufficient period of time so that the pump rate and hydraulic pressure may fracture the subterranean formations. Suitable crosslinked gel stabilizers previously used include, but are not necessarily limited to, sodium thiosulfate, diethanolamine, triethanolamine, methanol, hydroxyethylglycine, tetraethylenepentamine, ethylenediamine and mixtures thereof.

Additional common additives for fracturing fluids are enzyme breaker (protein) stabilizers. These compounds stabilize the enzymes and/or proteins used in the fracturing fluids to eventually break the gel after the subterranean formation is fractured so that they are still effective at the time it is desired to break the gel. If the enzymes degrade too early they will not be available to effectively break the gel at the appropriate time. Examples of enzyme breaker stabilizers commonly incorporated into fracturing fluids include, but are not necessarily limited to sorbitol, mannitol, glycerol, citrates, aminocarboxylic acids and their salts (EDTA, DTPA, NTA, etc.), phosphonates, sulphonates and mixtures thereof.

It has become desirable to fracture a well, break the gel as in a conventional fracturing treatment, but keep the broken fracturing fluid within the formation for a relatively long period of time, for instance at least one month or up to nine months or longer. However, leaving the fracturing fluid composition within the formation presents additional concerns, such as oil wetting of the formation by the fluid, increasing the water saturation or water blocking by the fluid, disturbing the clay particles within the formation and inducing clay swelling or clay migration which will result in reservoir permeability damage, souring of the reservoir crude (which is caused by H_2S generation by *in situ* sulfate-reducing bacteria), reservoir plugging (slime biopolymers generated by *in situ* microbes) and inorganic scale deposition (such as barium sulfate). It would be helpful if multifunctional fracturing fluid compositions could be devised that have suitable

properties or characteristics that would permit the fracturing fluid to remain in the formation for extended periods of time.

Summary of the Invention

Accordingly, it is an object of the present invention to provide a multifunctional fracturing fluid that may be left in a fractured formation for an extended period of time.

It is another object of the present invention to provide a multifunctional fracturing fluid that prevents oil wetting of the formation.

Another object of the invention is to provide a multifunctional fracturing fluid that is inhibited in its tendency to water block the formation.

Another objective of the invention is to provide a multifunctional fracturing fluid that inhibits clay swelling and/or migration formation damage.

Yet another object of the invention to provide a multifunctional fracturing fluid that is inhibited in its tendency to generate H_2S.

Still another object of the present invention to provide a multifunctional fracturing fluid that is inhibited in its inclination to plug the reservoir with slime biopolymers.

One other object of the present invention is to provide a fracturing fluid that will inhibit inorganic scale depositions of calcium or barium sulfate scales.

In carrying out these and other objects of the invention, there is provided, in one form, A method for fracturing a subterranean formation that involves first pumping a fracturing fluid composition down a wellbore to a subterranean formation. The fracturing fluid composition is permitted to gel, although the time frame for gel formation could begin while the composition is being pumped down the wellbore, and may continue while fracturing occurs. The fracturing fluid composition is then pumped against the subterranean formation at sufficient rate and pressure to fracture the formation. The fracturing fluid composition gel is substantially broken after fracturing has taken place. The broken fracturing fluid composition is then left in the formation for a relatively extended period of time, in one non-limiting example, at least 28

days. Subsequently the fracturing fluid composition is flowed out of the formation.

The multifunctional fracturing fluid composition useful in the method described immediately above may include, in one non-limiting embodiment of the invention, at least one hydratable polymer, at least one water wetting control agent, at least one clay control agent, at least one microbe growth control agent, at least one scale inhibitor, and at least one breaking agent.

Detailed Description of the Invention

Polymer-based fracturing fluid systems have been discovered for use in oil and gas well fracturing treatments where the fracturing fluid is to remain within the formation for a period of time greater than 28 days. At least two embodiments are envisioned. One system would be an anti-bacterial-based formulation, while the other would be a bacteria-based formulation. Both systems would control or prevent the potential of the fracturing fluid composition from oil wetting the fractured subterranean formation (prevent an increase in oil saturation). In addition, both systems would also manage the tendency of the fracturing fluid composition to adversely alter the water saturation of the formation, to prevent a decrease in water saturation commonly known as water block – another undesirable event. Both systems would also prevent clay induced formation damage, such as clay migration and pore throat reservoir plugging. Reservoir crude souring, or the generation of hydrogen sulfide (H_2S) by *in situ* sulfate-reducing bacteria would also be inhibited by both embodiments of the inventive composition. Both embodiments of the invention would be expected to control reservoir plugging, such as that caused by slime biopolymers generated by *in situ* microbes. Additionally, both embodiments of the invention would be expected to control reservoir plugging, such as that caused by inorganic scale deposits, such as barium sulfate

The fracturing method using the fracturing fluid compositions of the invention proceeds essentially conventionally and includes, but is not limited to the following procedure:

a. Pumping a fracturing fluid composition down a wellbore to a subterranean formation;
b. Permitting the fracturing fluid composition to gel;
c. Pumping the fracturing fluid composition against the subterranean formation at sufficient rate and pressure to fracture the formation;
d. Breaking the fracturing fluid composition gel;
e. Leaving the fracturing fluid composition in the formation for a relatively extended period of time; and
f. Subsequently flowing the fracturing fluid composition out of the formation.

By leaving the fracturing fluid in the formation for a relatively extended period of time is meant that the fluid whose gel has been broken is not flowed back out of the well bore (or produced) relatively soon or even immediately after the gel is broken. In one non-limiting embodiment of the invention, the fracturing fluid having reduced viscosity is left in the formation at least 28 days. The broken fluid could remain in the formation up to nine months or longer.

The fracturing fluid composition of the invention has the following general formula:

i) at least one hydratable polymer;
ii) at least one water wetting control agent;
iii) at least one salt clay control agent;
iv) at least one microbe growth control agent;
v) at least one scale inhibitor;
vi) at least one breaking agent;
vii) optionally, an organic clay control agent; and
viii) optionally, at least one biocide.

Of course, like most fracturing fluids, these contain water as a primary component, making up the remainder of the composition.

It is very difficult to determine with precision and in advance what the optimum proportion of the components of the fracturing fluid composition of this invention will be due to a number of complex, interrelated factors including, but not limited to, the structure of the formation, the temperature and pressure of

the formation, the hydrocarbon and/or water mixture within the formation, the design of the fracturing job, the particular components used in the fracturing fluid, etc. Nevertheless, in an effort to give some indication of suitable proportions of the various components of the inventive formulation, the components may have the broad and preferred proportional ranges shown in Table I, in one non-limiting embodiment. The proportions are based on the total fracturing fluid composition.

TABLE I

Component	Broad range	Preferred range
Hydratable polymer	0.12 to 0.75 %bw	0.24 to 0.6 %bw
Water wetting control agent	0.05 to 3.0 %bv	0.1 to 1.0 %bv
Additional water wetting agent/ mutual solvent	0.05 to 5.0 %bv	0.2 to 2.0 %bv
Salt Clay control agent	0.5 to 12.0 %bw	2.0 to 7.0 %bw
Additional clay control agent	0.05 to 1.0% bv	0.2 to 0.4% bv
Microbe growth control agent	0.001 to 2.0 %bw	0.024 to 0.36 %bw
Scale inhibitor	0.05 to 1.0 %bv	0.1 to 0.2 %bv
Demulsifier control agent	0.05 to 1.0% bv	0.2 to 0.5 %bv
Breaking agent	0.0001 to 0.72 %bw	0.012 to 0.12 %bw
Additional Biocide	0.001 to 1.0 %bv	0.05 to 0.2 %bv

The total clay control agent may preferably range from 1.0 to 8.0%bv in one non-limiting embodiment of the invention. In another non-limiting embodiment of the invention, the microbe growth control agent preferably ranges from 0.01 to 0.72%bw. An intermediate range for the scale inhibitor is from 0.05 to 0.5%bv in another non-limiting embodiment of the invention. In a still further non-limiting embodiment of the invention, the breaking agent ranges from 0.0001 to 0.48%bw as an intermediate range.

The hydratable polymer may be a polysaccharide, in one non-limiting embodiment of the invention, such as guar, hydroxypropylguar, carboxymethyl guar, carboxymethyl hydroxypropyl guar, and other guar polymer derivatives. The hydratable polymer may be cross-linked, such as by using borate, titanate or zirconate ions, or complexes or combinations thereof. One non-limiting example would be soluble and sparingly soluble boron minerals, such as borax, ulexite, and colemanite minerals. Another non-limiting example would be the use of organically complexed borates, titanates, or zirconates, such as borate ions complexed onto polyol compounds such as sorbitol, mannitol, sodium gluconate, and the like, to name some non-limiting examples. Hydrating, gelling and crosslinking the polymers would occur as is conventionally known in the art.

The water wetting control agent would be any material that would control water wetting of the formation. Suitable water wetting control agents include, but are not necessarily limited to, any water-wetting (rather than oil-wetting) surfactant and solvents such as ST-100 or ST-101 (both available from Mayco Wellchem, Inc.), ethylene glycol monobutyl ether (EGMBE), diethylene monomethyl glycol ether, methyl pyrrolidone, alcohols (such as isopropanol and ethanol), anionic surfactants such as alkyl sulfates or sulphonates, alkyl carboxylates, alkyl succinates, and alkyl phosphates or phosphonates; non-ionic surfactants such as alkyl glucosides, ethoxylated or propoxylated alkyls or alcohols; and amphoteric surfactants such as amine oxides, alkyl acetates, alkyl propionates, and alkyl betaines, and mixtures thereof. For the practice of this invention, sulfur-containing compounds generally should not be used in the invention.

Suitable clay control agents include, but are not necessarily limited to, potassium chloride (KCl), tetramethylammonium chloride (TMAC), CS-6 (available from Special Products), ammonium chloride, calcium chloride, magnesium chloride, alkyl quaternary amines, alkyl benzyl quaternary amines, polymeric products having multivalent ions and mixtures thereof.

In general, most all of the components from the fracturing fluid composition of the invention should not contain sulfur because *in situ* sulfate-reducing

bacteria may digest the molecules and produce hydrogen sulfide with the sulfur. The exception is the use of sulfur in surfactants, particularly in alkyl benzyl sulphonate surfactants since the sulfur in this form is typically more stable. Toward this end, no persulfate breakers should be used in the fracturing fluids, including any encapsulated persulfates. Additionally, no thiosulfate high temperature gel stabilizers should be employed. Instead, if high temperature stability is desired or needed, it is suggested that triethanolamine (TEA) be used, a known polymer stabilizer for high temperature crosslink stability applications. TEA is available as N-140 from Brenntag. Other suitable non-sulfur containing high temperature gel stabilizers include, but are not necessarily limited to, methanol, diethanolamine, ethylenediamine, n-butylamine, and mixtures thereof.

In situ microbe control can also be positively accomplished by including bacteria that compete with the *in situ* bacteria for non-polymer nutrients. Such bacteria include, but are not limited to, *Pseudomonas Aeruginosa Esmeralda, Pseudomonas Florescens, Pseudomonas Putidas, Serretia Marscens, Enterobacter Ecolacae, Nitrobactor Vulgaris, Nitrosomonas Europaea, Clostridium Pasteurianum, Bacillus Thuringiensis, Bacillus Stearothermophilus, Bacillus AB-2, Corynebacterium Insidiosum, Rhodococcus ST-5*, and combinations thereof. In one non-limiting embodiment, these bacteria would be present in the fracturing fluids in amounts of 0.5 to 1.0 by volume (bv).

Further, in both embodiments of the invention, control of sulfate-reducing bacteria (to prevent H_2S crude souring) and control of bio-polysaccharide (slime) production by *in situ* microbes may be controlled by including one or more components from the following list, which include, but are not necessarily limited to, potassium nitrate, sodium nitrate, sodium phosphates, ammonium nitrate, ammonium phosphate, sodium chlorate, sodium bromate, sesquicarbonate, potassium iodate, potassium iodide, potassium iodine, sodium iodate, sodium iodide, methanol, ethanol, isopropanol, butanol, sodium carbonate, sodium bicarbonate, sodium salicylate, phenolic compounds, triclosan, benadine (polyvinylpyrrolidone-iodine iodophor), other iodophors, potassium bromate, potassium perchlorate,

potassium nitrite, potassium chlorate, periodates, ammonium bromide, sodium bromide, sodium nitrite, potassium bromide, calcium bromide, zinc bromide, hypochlorites, sodium chlorite, potassium chlorite, hydroxymethyl glycinate, metal complex polyols or amino acids (such as copper gluconate, copper glycinate, copper aspartate), quaternary ammonium compounds, and mixtures thereof.

Suitable conventional scale inhibitors include, but are not necessarily limited to SWC-203 (available from Baker Oil Tools), polyaspartates, imidosuccinates, polycarboxylics, organophosphonates, organocarboxylates, acrylates, acrylamides, succinates, gluconates, and mixtures thereof. Such scale inhibitors are employed to prevent potential scale build up when the fracturing fluid and the formation brine completely commingle over the extended time period.

Various known breaker aids may also be employed, including but not necessarily limited to, amines and amino compounds (such as triethylene glycol diamine and arginine), metal complexes (such as copper EDTA and copper gluconate), sorbitol, sodium sesquicarbonate, mannitol, gluconates, chlorites, hypochlorites, chlorates, perchlorates, hypochlorates, percarbonates, bromates, peroxides, periodates, and mixtures thereof.

In the anti-bacterial embodiment of the fracturing fluid composition of the invention, surfactant agents may include thermally stable or thermally unstable quaternary amines that serve as a long term or temporary biocide. Such biocides would be unsuitable for the bacterial embodiment of the fracturing fluid composition because they would destroy the useful bacteria intentionally incorporated into the formulation, as will be described later. Suitable quaternary amines for this purpose include, but are not necessarily limited to, cocodimethyl ammonium chloride, dodecyldimethyl ammonium chloride, alkyldimethylbenzyl ammonium chloride, dialkyldimethylbenzyl ammonium chloride, and mixtures thereof. Additionally the oxyhalogen compounds usable as breakers can also serve as biocidal agents in the anti-bacterial embodiment.

Also in the anti-bacterial embodiment of the fracturing fluid composition of the invention, microbe growth inhibition may be achieved by including a

metal ion such as zinc, tin, copper, cobalt, antimony, beryllium, cadmium, chromium, copper, nickel, selenium or silver ions. Suitable sources of copper, silver, and other ions include, but are not necessarily limited to, copper or silver chelated to tetrasodium ethylenediaminetetracetic acid (Na_4EDTA) or to other aminocarboxylic acids, copper or silver complexed to chitosan and chitosan derivatives, copper or silver complexed to polyols such as gluconate or glucoheptonate, copper, cobalt, or silver complexed to amino acids or metalloproteins, copper or silver naphthenate, copper or silver quinolinolate, and copper carbonate and mixtures thereof. Additionally in this embodiment, oxidizer breakers may be used to break or reduce the viscosity of the fracturing fluid after the formation is fractured.

Suitable oxidizer breakers include, but are not necessarily limited to, sodium percarbonate, sodium bromate, sodium chlorite, sodium chlorate, sodium perchlorate, potassium chlorite, potassium chlorate, potassium perchlorate, potassium chlorite, hypochlorites, calcium and magnesium peroxides, sodium or potassium nitrite, sodium or potassium nitrate, periodates, and mixtures thereof.

In the bacteria formulation embodiment of the invention, the breakers for the gels after fracturing may include bacteria and enzymes, as are well known in the art. Suitable bacteria breakers include, but are not necessarily limited to, polysaccharide decomposing (eating or digesting) bacteria, such as thermophillic, barophillic, and/or non-biopolymer (slime) generating types of bacteria or microbes, which include, but are not necessarily limited to, *Bacillus Subtilis, Bacillus Licheniformis, Bacillus Circulans, Pseudomonas Putida, Pseudomonas Florescens, Candida Albicans, Aspergillus Niger, Aspergillus Oryzae, Enterococcus Faecium, Corynebacterium, Clostridium ATCC #53797 and other species, Streptomyces species, Rhodococcus species, Anthrobacter species, Nocardia species,* and mixtures thereof. In one non-limiting embodiment of the invention, such gel breaking bacteria or microbes are used in a proportion of 0.1 to 1.0% bv. With respect to enzyme breakers, suitable enzymes include, but are not necessarily limited to, GBW-174L (available from BIO-CAT, Inc.), PLEXIGEL 10L (available from Chemplex), HC-70 (available from Chemgen),

GAMMANASE 1.0L (available from Novozymes), and any cellulase and hemicellulase enzyme breaker, amylases, pectinases, and xylanases, and mixtures thereof when used in formations having a temperature below 200°F (93°C). Sodium bromate or other known breakers such as chlorites, chlorates, hypochlorites, hypochlorates, calcium peroxide, magnesium peroxide, and aminocarboxylic acids (such as Na_3HEDTA and Na_3NTA), may be used when the formation temperature is 200°F (93°C) or above. Any of the breakers for the bacterial embodiment of the fracturing fluid or the anti-bacterial embodiment of the fluid may be employed in encapsulated form to delay their contact with the gel and thus delay gel breaking.

The invention will now be further illustrated with respect to certain specific examples which are not intended to limit the invention, but rather to provide more specific embodiments as only a few of many possible embodiments.

EXAMPLE 1

Anti-Bacterial Formulation

One embodiment of a polymer-based anti-bacterial fracturing fluid composition may be as follows:

1. From 0.001 to 1.0 % bw (by weight) fracturing polymers and crosslinkers; in one embodiment, preferably a borate crosslinked guar.
2. From 0.05 to 0.5 % bv of a thermally stable quaternary amine biocide (such as EC-9555A by Nalco/Exxon).
3. From 1.0 to 200 ppm copper ions (*e.g.* Na_4EDTA chelated copper chloride) and from 0.01 to 0.5 % bw benadine (PVP-iodine iodophor by BASF) for microbe growth inhibition.
4. From 0.1 to 1.0 % bv ST-100 and/or EGMBE for water wetting control.
5. Approximately 7% bw KCl, 0.5% bv TMAC, and 0.3% bv CS-6 clay control agents.
6. *In situ* microbe control agents:
    a. No persulfate breakers (including no encapsulated form).
    b. No thiosulfate high temperature gel stabilizer (N-140 (TEA) may be used for high temperature stability).

c. From 0.01 to 0.5 % bw sodium nitrate, ammonium phosphate, sodium bromate, and sesquicarbonate for sulfate-reducing bacteria control (no H_2S crude souring) and control of bio-polysaccharide (slime) production by *in situ* microbes.

7. From 0.1 to 0.5 % bv SCW-203 scale inhibitor.

8. From 0.0001 to 0.25 % bw sorbitol and/or sodium sesquicarbonate as breaker aids.

9. From 0.0001 to 0.25 % bw sodium percarbonate, sodium bromate, or sodium chlorite oxidizer breakers.

EXAMPLE 2

Bacteria Formulation

One embodiment of a polymer-based bacteria fracturing fluid composition may be as follows:

1. From 0.001 to 1.0 % bw fracturing polymers and crosslinkers; in one embodiment, preferably a borate crosslinked guar.

2. Approximately 7% KCl, 0.5% TMAC, and 0.3% CS-7 clay control agents.

3. From 0.1 to 1.0 % bv ST-100 and 0.3 to 1.0% bv EGMBE for water wetting control.

4. 1.0% bv polysaccharide eating/decomposing bacterial, *e.g.* thermophillic, barophillic, and non-biopolymer (slime) generating types of bacteria, such as *Bacillus Licheniformis, Clostridium species such as ATCC #53797*, and FRAC-BAC I and FRAC-BAC II bacteria solutions by Micro-Bac, Round Rock, TX.

5. Approximately 0.2 to 1.2% bw maltose sugar.

6. *In situ* microbe control agents:

a. Approximately 0.5% bv *Pseudomonas Aeruginosa Esmeralda* and *Pseudomonas Florescens* bacteria (by Micro-TES, Inc., San Antonio, TX)

b. No persulfate breakers (including no encapsulated form).

c. No thiosulfate high temperature gel stabilizer (N-140 (TEA) may be used for high temperature stability).

d. From 0.01 to 0.5 % bw sodium nitrate, ammonium phosphate, sodium bromate, and sesquicarbonate for sulfate-reducing bacteria control (no H_2S crude souring) and control of bio-polysaccharide (slime) production by *in situ* microbes.

7. From 0.1 to 0.5 % bv SCW-203 scale inhibitor.

8. From 0.0001 to 0.5 % bw sorbitol and/or sodium sesquicarbonate as breaker aids.

9. From 0.001 to 5.0 % bv GBW-174L (BIO-CAT, Inc.), PLEXIGEL 10L (by Chemplex, Snyder, TX), HC-70 (by Chemgen) or GAMMANASE 1.0L (by Novozymes) enzyme breakers for formations up to 200°F (93°C); from 0.01 to 0.25 % bw Na_3HEDTA, Na_3NTA, or calcium peroxide for formations at 200°F (93°C) and above.

EXAMPLE 3

Bacteria Formulation

One embodiment of a polymer-based bacteria fracturing fluid composition may be as follows:

1. From 0.001 to 1.0 % bw fracturing polymers and crosslinkers; in one embodiment, preferably a borate crosslinked guar.

2. Approximately 2.0 to 7.0% bw KCl, 0.2% TMAC, and 0.4% Claprotek CF (by CESI Chemicals, Marlow, OK) clay control agents.

3. From 0.2 to 0.4 % bv ST-100 and 0.5 to 2.0% bv EGMBE for water wetting control.

4. Approximately 0.5 to 2.0% bv Paragone E (bacteria solution from Micro-TES, Inc., San Antonio, TX) high molecular weight crude oil upgrading and polysaccharide eating/decomposing bacteria: *e.g.* thermophillic and barophillic non-biopolymer (slime) generating + high molecular weight paraffin decomposing types of bacteria composition.

5. *In situ* microbe control agents:

a. No persulfate breakers (including no encapsulated form).

b. No thiosulfate high temperature gel stabilizer (N-140 (TEA) may be used for high temperature stability).

c. From 0.01 to 0.5 % bw sodium nitrate, ammonium phosphate, and sesquicarbonate for sulfate-reducing bacteria control (no H_2S crude souring) and control of bio-polysaccharide (slime) production by *in situ* microbes.

6. From 0.2 to 0.5 % bv SCW-203 scale inhibitor.

7. From 0.0001 to 0.5 % bv glucose (62/43 Corn Syrup by ADM Corporation) or sorbitol (Sorbo by SPI Polyols) as breaker aids.

8. From 0.001 to 5.0 % bv GBW-174L (by BIO-CAT, Inc.), PLEXIGEL 10L (by Chemplex, Snyder, TX), HC-70 (by Chemgen) or GAMMANASE 1.0L (by Novozymes) enzyme breakers for formations up to 200°F (93°C); from 0.01 to 0.25 % bw Na_3HEDTA, Na_3NTA for formations at 200°F (93°C) and above.

EXAMPLE 4

Anti-Bacterial Formulation

One embodiment of a polymer-based anti-bacterial fracturing fluid composition may be as follows:

1. From 0.001 to 1.0 % bw (by weight) fracturing polymers and crosslinkers; in one embodiment, preferably a borate crosslinked guar.

2. From 1 to 5% bw potassium chloride clay control agent.

3. From 0.05 to 0.2 % bv of a thermally stable quaternary amine biocide (EC-9555A by Nalco/Exxon).

4. From 0.1 to 0.4 % bv AG-6206 (alkyl glucoside by Akzo Nobel) and 0.5 to 2.0% bv EGMBE for water wetting control.

5. From 0.2 to 0.5% bv NE-100 demulsifier.

6. Approximately 0.2% bv TMAC control agent.

7. *In situ* microbe control agents:

a. No persulfate breakers (including no encapsulated form).

b. No thiosulfate high temperature gel stabilizer (N-140 (TEA) may be used for high temperature stability).

c. From 0.1 to 0.5 % bv sodium hypochlorite (industrial grade solution) and from 0.1 to 0.5% bw sodium bromide for sulfate-reducing

bacteria control (no H_2S crude souring) and control of bio-polysaccharide (slime) production by *in situ* microbes.

8. From 0.1 to 0.5 % bv SCW-203 scale inhibitor.

9. From 0.01 to 0.2 % bw sodium gluconate and/or sodium glucoheptonate as breaker aids.

10. From 0.0001 to 0.25 % bw sodium percarbonate, sodium bromate, or sodium chlorite oxidizer breakers.

EXAMPLE 5

Anti-Bacterial Formulation

One embodiment of a polymer-based anti-bacterial fracturing fluid composition may be as follows:

1. From 0.001 to 1.0 % bw (by weight) fracturing polymers and crosslinkers; in one embodiment, preferably a borate crosslinked guar.

2. From 2 to 7% bw potassium chloride clay control agent.

3. From 0.05 to 0.2 % bv of sodium hypochlorite (industrial grade solution) biocide.

4. From 0.1 to 1.0 % bv Simulsol SL 11W (alkyl glucoside by SEPPIC, a subsidiary of Air Liquide) and 0.2 to 1.0% bv M-PYROL (methyl pyrrolidone by ISP Technologies) for water wetting control.

5. From 0.1 to 0.5% bv NE-200E demulsifier.

6. Approximately 0.2% to 1.0% bv Claprotek CF (choline bicarbonate by CESI Chemical, Marlow, OK) clay control agent.

7. *In situ* microbe control agents:

   a. No persulfate breakers (including no encapsulated form).

   b. No thiosulfate high temperature gel stabilizer (hexamethylenediamine (by DuPont Intermediates & Specialties) may be used for high temperature stability).

   c. From 0.01 to 0.5 % bw sodium chlorite and from 0.1 to 0.5% sodium bromide for sulfate-reducing bacteria control (no H_2S crude souring) and control of bio-polysaccharide (slime) production by *in situ* microbes.

8. From 0.1 to 0.5 % bv sodium iminodisuccinate (Baypure CX-100/34% by Bayer Chemicals) scale inhibitor.

9. From 0.01 to 0.2 % bv glucose (62/43 Corn Syrup by ADM Corporation) and/or sorbitol (Sorbo by SPI Polyols) as breaker aids.

10. From 0.05 to 1.0 % bv sodium hypochlorite oxidizer breaker.

EXAMPLE 6

Anti-Bacterial Formulation

One embodiment of a polymer-based anti-bacterial fracturing fluid composition may be as follows:

1. From 0.001 to 1.0 % bw (by weight) fracturing polymers and crosslinkers; in one embodiment, preferably a borate crosslinked guar.

2. From 2 to 5% bw potassium chloride clay control agent.

3. From 0.1 to 0.4 % bv of SP-82 (from Special Products) surfactant/biocide.

4. From 0.1 to 0.2 % bv AG-6206 (alkyl glucoside by Akzo Nobel) and 0.5 to 1.0% EGMBE for water wetting control.

5. From 0.012 to 0.06% bw Stim-440 (by Mayco Welchem, Houston) demulsifier.

6. Approximately 0.2% TMAC and 0.5% bv Claprotek CF (by CESI Chemical, Marlow, OK) clay control agents.

7. *In situ* microbe control agents:

   a. No persulfate breakers (including no encapsulated form).

   b. No thiosulfate high temperature gel stabilizer (hexamethylenediamine (by DuPont Intermediates & Specialties) may be used for high temperature stability).

   c. From 0.1 to 0.2 % bv sodium hypochlorite (industrial grade solution) and from 0.05 to 0.1% bw sodium bromide for sulfate-reducing bacteria control (no H_2S crude souring) and control of bio-polysaccharide (slime) production by *in situ* microbes.

8. From 0.1 to 0.5 % bv sodium iminodisuccinate (Baypure CX-100/34% by Bayer Chemicals) scale inhibitor.

9. From 0.01 to 0.2 % bw sodium gluconate or 0.05 to 0.3% bv sodium glucoheptonate (ES-50 by C.P. Hall Chemicals) as breaker aids.

10. From 0.0001 to 0.25 % bw sodium percarbonate, sodium bromate, or sodium chlorite oxidizer breakers.

In the foregoing specification, the invention has been described with reference to specific embodiments thereof, and is expected to be demonstrated as effective in providing fracturing fluid compositions which can remain in the formation for a relatively long time after the formation is fractured and the gel broken before being produced or flowed back. However, it will be evident that various modifications and changes can be made to the fracturing fluid compositions of this invention without departing from the broader spirit or scope of the invention as set forth in the appended claims. Accordingly, the specification is to be regarded in an illustrative rather than a restrictive sense. For example, specific combinations of agents and components, and proportions of these agents and components, falling within the claimed parameters, but not specifically identified or tried in particular compositions, are anticipated and expected to be within the scope of this invention.

What is claimed is:

1. A method for fracturing a subterranean formation comprising:
   a. pumping a fracturing fluid composition down a wellbore to a subterranean formation;
   b. permitting the fracturing fluid composition to gel;
   c. pumping the fracturing fluid composition against the subterranean formation at sufficient rate and pressure to fracture the formation;
   d. breaking the fracturing fluid composition gel;
   e. leaving the fracturing fluid composition in the formation for at least 28 days; and
   f. subsequently flowing the fracturing fluid composition out of the formation;

where the fracturing fluid composition comprises:

   i) at least one hydratable polymer;
   ii) at least one water wetting control agent;
   iii) at least one clay control agent;
   iv) at least one microbe growth control agent;
   v) at least one scale inhibitor; and
   vi) at least one breaking agent.

2. The method of claim 1 where in the fracturing fluid composition there is an absence of components that contain sulfur, except for sulphonates.

3. The method of claim 1 or 2 where the fracturing fluid composition further comprises a crosslinking agent.

4. The method of claim 3 where in the fracturing fluid composition the hydratable polymer is guar and where the crosslinking agent is borate ion.

5. The method of any one of claims 1 through 4 where the fracturing fluid composition is an anti-bacterial formulation and the composition further comprises a biocide.

6. The method of any one of claims 1 through 4 where the fracturing fluid composition is a bacterial formulation, the hydratable polymer is a polysaccharide and the composition further comprises at least one polysaccharide-decomposing bacteria.

7. The method of any one of claims 1 through 6, where the fracturing fluid composition comprises:

i) from 0.12 to 0.75%bw of at least one hydratable polymer;
ii) from 0.05 to 3.0%bv of at least one water wetting control agent;
iii) from 0.5 to 12.0%bw of at least one clay control agent;
iv) from 0.001 to 2.0%bw of at least one microbe growth control agent;
v) from 0.05 to 1.0%bv of at least one scale inhibitor;
vi) from 0.0001 to 0.72%bw of at least one breaking agent; and
vii) at least one crosslinking agent

where all proportions are based on the total fracturing fluid composition.

8. A fracturing fluid composition comprising:

i) at least one hydratable polymer;
ii) at least one water wetting control agent;
iii) at least one clay control agent;
iv) at least one microbe growth control agent;
v) at least one scale inhibitor; and
vi) at least one breaking agent.

9. The fracturing fluid composition of claim 8 where there is an absence of components that contain sulfur, except for sulphonates.

10. The fracturing fluid composition of claim 8 or 9 further comprises a crosslinking agent.

11. The fracturing fluid composition of claim 10 where the hydratable polymer is guar and where the crosslinking agent is borate ion.

12. The fracturing fluid composition of any one of claims 8 through 11 where the composition is an anti-bacterial formulation and the composition further comprises a biocide.

13. The fracturing fluid composition of any one of claims 8 through 11 where the composition is a bacterial formulation, the hydratable polymer is a polysaccharide and the composition further comprises at least one polysaccharide-decomposing bacteria.

14. The fracturing fluid composition of any one of claims 8 through 11 further comprising:

i) from 0.12 to 0.75%bw of at least one hydratable polymer;
ii) from 0.05 to 3.0%bv of at least one water wetting control agent;
iii) from 0.5 to 12.0%bw of at least one clay control agent;
iv) from 0.001 to 2.0%bw of at least one microbe growth control agent;
v) from 0.05 to 1.0%bv of at least one scale inhibitor; and
vi) from 0.0001 to 0.72%bw of at least one breaking agent;

where all proportions are based on the total fracturing fluid composition.

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Application No: GB 0226321.8 **Examiner:** Kathryn Orme
Claims searched: 1-14 **Date of search:** 30 April 2003

Patents Act 1977 : Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance	
X	8-14	GB 2377238 A	(BAKER HUGHES) see especially page 9 line 29 to page 10 line 21, page 11 lines 4-16, page 12 lines 15-18 and page 14 lines 9-19
X	8-12 & 14	EP 0540204 A2	(EXXON CHEMICAL) see especially page 6 lines 21-38
X, E	8-13	WO 02/070862 A1	(SCHLUMBERGER) see especially paragraphs 0025, 0027, 0038, 0041, 0043, 0047, 0048 and 0061
X	8-12 & 14	US 6227295 B1	(SCHLUMBERGER) see especially column 3 lines 34-43, column 4 lines 1-13 and column 6 lines 25-38
X	8-12 & 14	US 6138760	(B J SERVICES) see especially column 3 lines 35-48, column 4 lines 17-21, column 8 lines 47-50, column 11 lines 36-50, column 17 lines 5-25 and Example 1
X	8-10, 12 & 14	US 5002125	(WESTERN CO. OF NORTH AMERICA) see especially column 4 lines 47-63, column 6 lines 26-31, column 9 lines 60-68, column 10 line 64 to column 11 line 4

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC[V]:

E1F

Worldwide search of patent documents classified in the following areas of the IPC[7]:

E21B

The following online and other databases have been used in the preparation of this search report:

WPI, EPODOC, PAJ